16   Solute Transport and Reactions in Salt-Affected Soils

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Modeling solute transport and reactions in salt- and sodium-affected soils can be considered as three simultaneous processes: (i) solute transport; (ii) precipitation-dissolution reactions; and (iii) cation exchange. Solute transport is the physical movement of ions by convective transport (water transport) and ion dispersion within the solvent system (due to concentration gradients). Precipitation-dissolution reactions are dominated by carbonate or lime and gypsum reactions. Mineral weathering reactions are important in special cases, but are not considered here. Cation exchange models usually consider only calcium (Ca), magnesium (Mg), and sodium (Na) exchange on the negatively charged soil surfaces. However, in some cases it may be necessary to consider potassium (K) exchange if K constitutes a substantial portion of the solute or exchangeable ions. These three processes will be discussed separately and will be presented as separate subroutines that can be called by water flow and plant growth models similar to that described in Ch. 11.

A short program that calculates the cation-exchange selectivity coefficients needed by the cation exchange subroutine is also explained and listed. Other reactions and interactions of importance to salt-affected soil management, which may need to be considered in special cases, are also discussed.

I. MODELING SOLUTE TRANSPORT

The solute transport subroutine was an expansion of Childs and Hanks' (1975) solute model. Two program listings for solute transport, one in FORTRAN and one in BASIC, are shown in Appendices 1 and 3. Soil water flow and root extraction is discussed in Ch. 11. To include solute flow, an additional equation has to be solved after water flow and root extraction is computed. Root extraction rates are dependent on the combined effects of matrix and osmotic potential. This is done by modifying Eq. [4] of Ch. 11 to include osmotic effects as:

$$A(z,t) = \frac{[H_{root} + R_z - h_{(z,t)} - s_{(z,t)}]\, RDF_{(z,t)}\, K}{\Delta z\, \Delta x} \qquad [1]$$

where $A(z,t)$ is the root extraction rate, H_{root} is the water potential in the root at the soil surface, R_z is the root resistance term, $h_{(z,t)}$ is the soil and water matric potential, $s_{(z,t)}$ is the osmotic potential of the soil solution, RDF is the fraction of roots in the z depth increment, and K is the hydraulic conductivity of the depth increment. This equation includes only osmotic effects. Specific ion effects are not considered. The osmotic potential is assumed to be related to the soil solution concentration by a constant conversion factor. If the soil solution concentration is measured in moles of charge per cubic meter, the conversion factor is 0.36 to convert to osmotic potential expressed as meters of water.

Another equation needed to solve solute flow is:

$$\delta \, (\theta C)/t = \frac{\delta}{\delta z} \, [D(\theta, q) \, C/z + qC] \qquad [2]$$

where θ is soil water content, C is solute concentration, t is time, z is depth, $D(\theta, q)$ is a combined diffusion and dispersion coefficient, and q is volumetric water flux computed from the solution of the water flow equation. Note that qC is the solute mass flow term and θC is the total salt content. The solution of the above equation is interrelated with water flow because θ and q are dependent on water content. The solution of Eq. [2] assumes that no salt is removed from the soil by plants. The initial solute concentration must be known, as well as solute characteristics at the upper and lower boundaries. These boundary conditions must be consistent with the water flow boundary conditions as described in the water flow subroutine. Equation [2] is solved by numerical approximation using a tri-diagonal matrix solution in the same manner as the water flow equation described in Ch. 11. The solution of Eq. [2] has a problem with numerical dispersion, which causes the solution to be dependent on the size of the depth and time steps. To minimize this problem, a more complete numerical approximation is used here than is used for water flow in Ch. 11 (Bresler, 1973).

Individual ion transport requires an array to include complete, solution ion concentrations at the soil surface (SF1–SF8 arrays) corresponding to the water flux information.

Childs and Hanks' (1975) water flow-salt transport method was expanded from moving bulk dissolved salt to independently moving Ca, Mg, Na, K, Cl, and SO_4 as nonreactive ions, and to calculating HCO_3 and CO_3. During water application to the soil surface, these ions are contained in the SF1 to SF8 arrays (SF1 = Ca, SF2 = Mg, etc.) and represent the soil surface flux of ions in the irrigation or rain water. There are twice as many elements in each SF1 array as in the V or surface water flux array. The elements of the V array are in pairs; the first element is the water flux direction and the second element is the flux duration given in hours. If, for example, the V array contained 1.0, 10.0, −0.04, and 240, the SF1 array would include two elements, such as 20.0 and 0.0. When the water flux reached 1.0 cm/h for 10 h, the Ca concentration in the water surface element would be 20 mmol/L.

This would be followed by 240 h of evapotranspiration at a rate of -0.04 cm/h and, since Ca will not evaporate from the soil surface, the Ca flux would be zero.

Arrays SS1 to SS8 were added to contain the initial solute ion concentration, at the beginning of each time step, as a function of depth. The SE1 to SE8 arrays were added, and contain the final solute concentration for the end of each time step, as a function of depth. The surface boundary conditions are determined by the water flux boundary conditions. It is assumed that there is no diffusion or salt flow across the soil surface boundary when water is evaporating. Thus, salt can accumulate during evaporation in the depth increment nearest the top, but not at the top since that is the boundary.

Solute flux for the bottom boundary conditions is also necessary and three conditions are provided for. The first is a constant water content (and matrix potential) for the bottom boundary, such as a water table. Solutes flow up or down depending on soil water flux. The net solute flow would depend on the water flow direction and solute concentration at the lower boundary. The second condition provided for in this model, but not in the water flow model of Ch. 11, is a unit hydraulic gradient. This would occur if the soil is quite wet and if steady downward water flow was established. Solute would then flow downward only, and the amount of solute flow would be governed by conditions above the bottom layer and not by the bottom. It would also not matter what concentration was assumed for the lower layer. The third condition is that of zero water flux. This situation would occur for dry subsoils when there was no leaching. All solutes would, thus, be contained in the layers above the bottom boundary.

II. MODELING LIME AND GYPSUM SOLUBILITY REACTIONS

Calcium carbonate (lime) and gypsum precipitation and dissolution reaction models for describing salt- and sodium-affected soil reactions have received considerable attention. Interaction between CO_2, CO_3, HCO_3, Ca, and pH are a major component of these reactions and are reviewed elsewhere (Robbins, 1985). Sulfate and gypsum reactions are also important in many salt-affected soils (Dutt et al., 1972; Tanji, 1969). The importance of these two kinds of reactions often requires simultaneous modeling of lime and gypsum in the same system (Nakayama, 1969; Robbins et al., 1980a). The chemical precipitation-dissolution model described here considers both lime and gypsum reactions.

The CHEM subroutine calls several functions and subroutines during its execution. Soil solution electrical conductivity (EC) is calculated from individual ion concentrations by the ECM3 subroutine (McNeal et al., 1970). A function called ACT calculates monovalent and divalent, mean ion activity coefficients by first calculating ionic strength as 0.0127 multiplied by the EC (Griffin & Jurinak, 1973) and then uses the Davies' equation to calculate the activity coefficients from the ionic strengths (Stumm & Morgan, 1970). The PRECIP subroutine determines the equilibrium status between

lime, gypsum, and the soil solution. It then calls the SINK subroutine to determine the amount of lime and/or gypsum that must be precipitated or dissolved to bring the solution phase into equilibrium with the solid phase. These are all short subroutines and are explained by comments at the beginning and throughout the computer listings. The cation exchange subroutine, XCHANG, is also called by the CHEM subroutine under certain conditions and is discussed in the next section.

The CHEM subroutine starts by converting the input ion concentration from millimoles/L to moles/L and estimates a value for HCO_3 ion concentration. Carbon dioxide partial pressure (PCO_2) is converted from percent CO_2 or kilopascals to atmospheres. Lime and gypsum are converted from a weight basis to a solution-concentration basis for ease of mass balance calculation. The ECM3 subroutine and the ACT function are then called to calculate activity coefficients for estimating ion activities. First approximations of ion activities, including H, are made prior to entering the chemical equilibrium loop. Within each loop cycle, new activity coefficients and new ion activities are calculated for Ca, Mg, Na, SO_4, H, HCO_3, and CO_3. The calculated activity values include activity-coefficient and ion-pairing corrections for soils above a pH of 6.5 that contain lime and possibly gypsum (Robbins et al., 1980a). At this point, the PRECIP subroutine is called and the solution phase is equilibrated with solid phase lime and, if present, gypsum. The PRECIP subroutine in turn calls SINK to complete this calculation. New Ca activities, and HCO_3 and CO_3 concentrations are calculated next. Then, a new EC value is calculated and compared with the previous EC value. If the EC has changed $<1.0\%$ then the program proceeds. Otherwise the equilibrium loop is run again to fine-tune the calculation. On leaving the chemistry equilibrium loop, pH is calculated and the option to call the XCHANG subroutine is exercised. If called, new values are returned for solution and exchangeable cation values. All ions, CO_2, and lime and gypsum values are then converted to their original units, and sodium adsorption ratio (SAR) and exchangeable sodium percentage (ESP) values are calculated. The computer then returns to the main program that called CHEM.

III. MODELING CATION EXCHANGE

The primary reason for modeling cation exchange processes in salt-affected soils concerns the necessity to predict changes in the ESP. The exchangeable cations in a given volume of medium- to fine-textured soils are usually about two orders of magnitude greater than in solution for sodic and slightly to moderately salty soils. This gives the exchangeable ions a tremendous buffering effect on the ion composition in salt-affected soils. The tendency for high exchangeable-sodium concentrations to induce poor physical conditions in soils is a function of ESP and EC (see Bresler et al., 1982 for a review). Models predicting exchangeable cations and ESP in salt-affected soils range in complexity from ESP equivalent to SAR (Jury et al., 1979) through a series of expressions discussed in detail by Oster and Sposito (1980).

An exact relationship between solution Na and other cations, and relationships between SAR and ESP, does not exist for all soils or for different solution compositions in equilibrium with a particular soil (Babcock & Schulz, 1963; Sposito & Mattigod, 1977; Robbins & Carter, 1983).

A three cation exchange model for Ca-Mg-Na exchange in salt-affected soils was used by Dutt et al. (1972). The model described here was expanded to predict Ca-Mg-Na-K exchange in order to include soils high in soluble and exchangeable K (Robbins et al., 1980a). When the irrigation water or the soil solution contains less than four times as much Na as K, on a molar basis, the four-cation-exchange calculation method should be used (Robbins, 1984). The XCHANG subroutine uses the following four equations as the basis of the model:

$$X_{Ca} = CEC\left[\frac{(Mg)^{1/2}}{(Ca)^{1/2}K1} + \frac{(Na)}{(Ca)^{1/2}K2} + \frac{(K)K3}{(Ca)^{1/2}} + 1 \right]^{-1} \qquad [3]$$

$$X_{Mg} = CEC\left[\frac{(Ca)^{1/2}K1}{(Mg)^{1/2}} + \frac{(Na)}{(Mg)^{1/2}K5} + \frac{(K)K4}{(Mg)^{1/2}} + 1 \right]^{-1} \qquad [4]$$

$$X_{Na} = CEC\left[\frac{(Ca)^{1/2}K2}{(Na)} + \frac{(Mg)^{1/2}K5}{(Na)} + \frac{(K)K6}{(Na)} + 1 \right]^{-1} \qquad [5]$$

$$X_K = CEC\left[\frac{(Ca)^{1/2}}{(K)K3} + \frac{(Mg)^{1/2}}{(K)K4} + \frac{(Na)}{(K)K6} + 1 \right]^{-1} \qquad [6]$$

where X_{Ca}, X_{Mg}, X_{Na}, and X_K are exchangeable cations (meq/100 g or mol$_c$/Kg), CEC is the cation exchange capacity, (Na), (Ca), (Mg), and (K) molar activities in solution, and the Ki terms are the selectivity coefficient. The Vanselow convention for cation exchange is used here (Robbins et al., 1980a; Sposito, 1977). This model assumes that the exchangeable cations' sum is equal to the CEC. Exchange reactions are assumed to be sufficiently rapid that reaction rates are ignored. This is probably satisfactory, since the soil is continually experiencing wetting and drying cycles. Cation molar activities are needed as input and are calculated by the CHEM subroutine. Exchange selectivity coefficients $K1$, $K2$ . . . $K6$ are calculated by the EXCOEF model described later. These coefficients vary from one soil to another, and are due to differences in clay mineralogy and possibly other factors.

The XCOEF program is listed with the subroutines. It is used to calculate cation-exchange selectivity coefficients needed by the XCHANG subroutine for those soils in which the coefficients are not available. Necessary input data are Ca, Mg, Na, K, Ca, SO$_4$, HCO$_3$, and CO$_3$ concentrations in saturation paste extracts, saturation paste pH, and exchangeable Ca, Mg, Na, and K, and CEC for the soils. Extract-solution ion-concentration data units

are entered as milliequivalent's per liter. When millimoles per liter units are used as input data, $Z2$, the conversion factor to convert to moles per liter, should be changed to equal 1000 rather than 2000. Exchangeable ion and CEC can be entered as milliequivalents per 100 grams, milliequivalents per kilogram, or millimoles of charge per kilogram as long as the units are consistent between exchangeable ions and CEC (Robbins and Carter, 1983). The same assumptions are used for this program as for the CHEM subroutine. The XCOEF program also uses the FUNCTION ACT and the ECM3 subroutines to calculate activity coefficients and solution EC. Sample input and output files are listed with the XCOEF program.

When using cation-exchange selectivity coefficients from the literature, care must be used to determine if cation concentrations or activities were used, as well as the equation form used to calculate the coefficients. Some values may be the reciprocal of the values produced by this subroutine. Other available coefficients will be less reliable if they were calculated from cation concentration data rather than cation activity data (Robbins & Carter, 1983).

Values for $K3$, $K4$, and $K6$ are not required when K is not being modeled. Other expressions containing K, such as XK, ACK, AK, TK, or SK in the XCHANG subroutine, can also be simplified to exclude these variables and any equations in which these variables are calculated can be removed when K exchange is not of interest.

In a steady state system, the ESP can be calculated as

$$ESP = 100(Na) \left[(Na) + K2(Ca)^{1/2} + K5(Mg)^{1/2} + K6(K)\right]^{-1} \quad [7]$$

when cation activities and selectivity coefficients are available (Robbins, 1984).

IV. CRITICAL ASSUMPTIONS

The solute transport subroutine calculates vertical ion movement in the soil profile and assumes that: (i) the ions are not taken up by plant roots; (ii) ions are concentrated in the zone of water uptake; (iii) water uptake rates are a function of matrix plus osmotic potential; (iv) each ion moves independently of the other ions; (v) salts move up from a water table with upward moving water when present; and (vi) salts accumulate in the surface depth increment during periods of water evaporation from the soil surface.

The chemical precipitation-dissolution model considers both lime and gypsum reactions and assumes that: (i) the soil contains lime; (ii) the soil solution pH is controlled by soil-atmosphere, CO_2 partial pressure and Ca ion activity; (iii) the soil solution is an open system with respect to CO_2, meaning that CO_2 can enter (from roots or other biological activity) or leave (with moving water or air) the system, and rather than that the system is in equilibrium with the atmosphere; (iv) these reactions are thermodynamically rather than rate controlled, because the soil moisture content is continually changing from wetting to drying or drying to wetting cycles, thus, the system is seldom at equilibrium; and (v) Henry's Law constant (KH) for

CO_2 is assumed to be independent of temperature and salt concentration. The Davies' equation is used to calculate single ion activity coefficients and is not valid for solutions more concentrated than 0.5 M (Stumm & Morgan, 1970). Solutions more concentrated than 0.5 M should be modeled by other methods (Van Luik & Jurinak, 1979).

The cation exchange subroutine is constructed on the assumption that: (i) the CEC is equal to the sum of the exchangeable cations; (ii) the CEC is independent of pH; (iii) independent of total solution ion concentration; and (iv) independent of the ratio of each soluble or exchangeable cation to the other cation species; (v) the exchange reaction rates are sufficiently fast that equilibrium can be assumed; and (vi) the selectivity coefficients are constant over the range of the conditions simulated. The XCOEF program used to calculate the cation exchange coefficients is based on the same assumptions as in XCHANG.

V. MODEL VALIDATION

The initial validation data for these subroutines were obtained from a lysimeter study using two calcareous soils from Emery County, Utah. Hunting silty clay loam (fine-silty, mixed, calcareous, mesic Aquic Ustifluvent) did not contain gypsum, while Penoyer loam (coarse-silty, mixed, calcareous, mesic Typic Torrifluvent) did. Low, medium, and high $CaSO_4$ irrigation-water treatments were applied to the soils at 0.10 and 0.25 leaching fractions. The 12 treatments were randomly replicated three times. Soil solution samples were taken through 100-kPa porous, ceramic cups inserted into the lysimeter sides at 0.25, 0.50, and 0.75 m below the soil surface. A sand covered drain was placed in the bottom of each lysimeter (Robbins & Willardson, 1980). The lysimeters were cropped with alfalfa (*Medicago sativa* L.) for water consumption and for concentrating ions in the soil solution (Robbins et al., 1980a, b). Only two treatments will be discussed here. Treatment A consisted of low Ca and SO_4 irrigation water applied at a 0.25 leaching fraction to the Penoyer soil (with 0.07 gypsum by weight). This treatment produced the greatest amount of gypsum dissolution of those used. Treatment B consisted of irrigating the Hunting soil (no gypsum) with the high Ca and SO_4 irrigation water at a 0.10 leaching fraction. This treatment produced the greatest amount of gypsum precipitation in the nongypsiferous soil.

For the lysimeter validation studies, the main program was designed so that one of three calculation-method options could be selected. Option 1 periodically printed the various ions without calculating any chemical or exchange reactions. Only ion transport and dispersion were calculated. Option 2 called the CHEM subroutine, and calculated lime and gypsum precipitation as affected by ion concentration and CO_2 partial pressure. Option 3 called the XCHANG subroutine in addition to the CHEM subroutine and calculated changes in solution and exchangeable ion as a result of changes in cation concentration and ratios in the solution flowing through the soil.

A leaching study conducted in field plots with and without a corn (*Zea mays* L.) crop was used to evaluate the complete model for sensitivity and accuracy by Dudley et al. (1981). Instrumented plots were established on a Millville silt loam (coarse silty, carbonatic, mesic Typic Haploxeroll) with fairly uniform physical properties to below 1.2 m. The five irrigation waters that were used had a variety of ion ratios and concentrations, and EC and SAR values. High and low Ca and SO_4 concentrations were provided to include conditions with and without gypsum precipitation. The cropped plots were irrigated as needed. The remaining plots were either irrigated and then covered with plastic between irrigations, or continuously ponded with low-salt water between irrigations of the high-salt waters to provide a steady state water regime. Solution samples were obtained through suction extractions at 0.15-, 0.30-, 0.60-, and 1.20-m depths. Tensiometers were placed at these depths to follow the matric potential changes. Soil water content was measured using access tubes and a neutron probe.

Individual Ca, Mg, Na, K, Cl, HCO_3, and SO_4 ion and EC concentrations were measured, and SAR was calculated and compared with the predicted values for the lysimeter and field plot studies. On completion of the leaching treatments, soil samples were taken from the lysimeters and several plots at the same depths that the extraction tubes were placed. Water and ammonium acetate extracts were made to determine soluble and exchangeable Ca, Mg, Na, and K concentrations. The six selectivity coefficients were calculated from these data for the three soils.

VI. SUMMARY

In the lysimeter study, Option 1 did not adequately predict EC (Fig. 16-1) or SAR (Fig. 16-2) of the soil solution for any of the treatments. Option 2 was usually better at predicting EC, but was only occasionally better than Option 1 at predicting SAR. Option 3 predicted these two parameters very well when the pH profile was properly adjusted (see Robbins et al., 1980a for more discussion).

Differences in the ability of the three options to predict EC and SAR under different soil and water conditions arise from the differences in types of reactions involving each ion, thus requiring consideration of each ion separately. The chloride ion was considered to be chemically nonreactive, thus the same results were obtained regardless of the calculation method used (Fig. 16-3a). The agreement between predicted and measured Cl concentrations for all treatments after 278 d of irrigation, indicated that the solute transport prediction subroutine was working correctly.

Chemical precipitation and dissolution reactions were required to predict SO_4 concentration when gypsum solubility became a factor. Sulfate was overestimated by Option 1 when gypsum was being precipitated, but Option 2 (data not shown) and Option 3 produced essentially the same results (Fig. 16-3b). Sulfate was underestimated for treatment A (data not shown) when

Fig. 16-1. Measured and calculated electrical conductivity (EC) values for Treatments A and B by solute transport only (1); solute transport and chemical precipitation (2); and solute transport, chemical precipitation, and cation exchange (3).
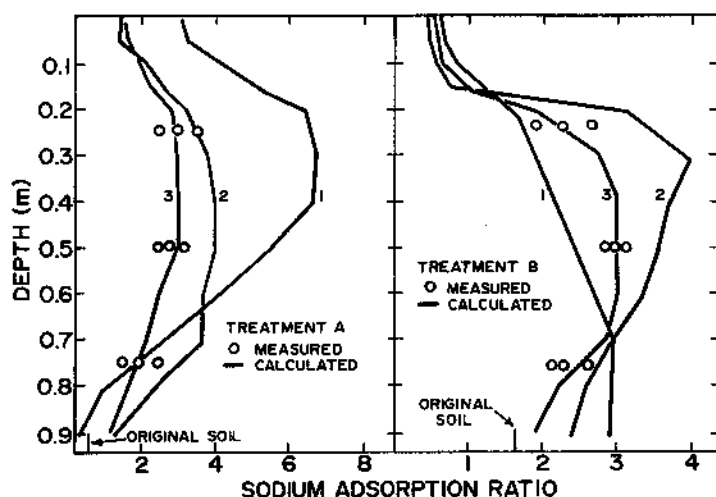
Fig. 16-2. Measured and calculated sodium adsorption ratio (SAR) values for Treatments A and B by solute transport only (1); solute transport and chemical precipitation (2); and solute transport, chemical precipitation, and cation exchange (3).

CHEM was not used, since gypsum was dissolving and releasing SO_4 into solution during irrigation with low SO_4 water.

Predicted Mg, Na, and K values are not affected by the CHEM subroutine alone. These are moved as inert ions by Options 1 and 2. Consequently, both options give the same results for these ions for all treatments. Neither Option 1 nor 2 adequately predicted any of the cations when their ratios or concentration in solution was not in equilibrium with the cation
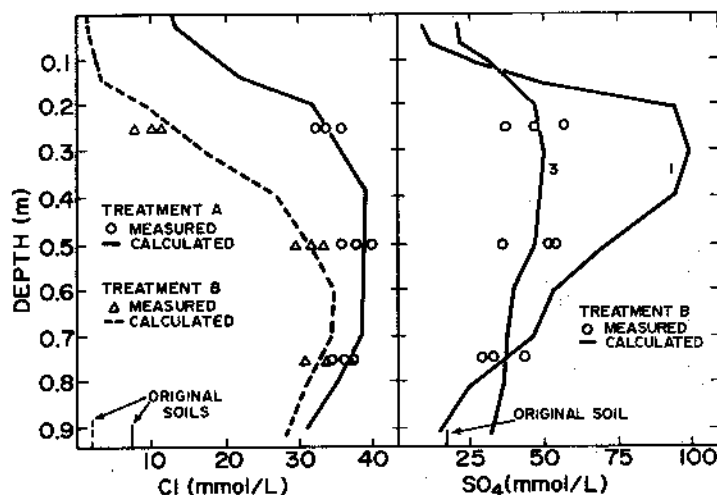
Fig. 16-3. Measured and calculated Cl concentrations for Treatments A and B by all three methods. Measured and calculated SO_4 concentrations by solute transport only (1); and solute transport, chemical precipitation, and cation exchange (3) for Treatment B.
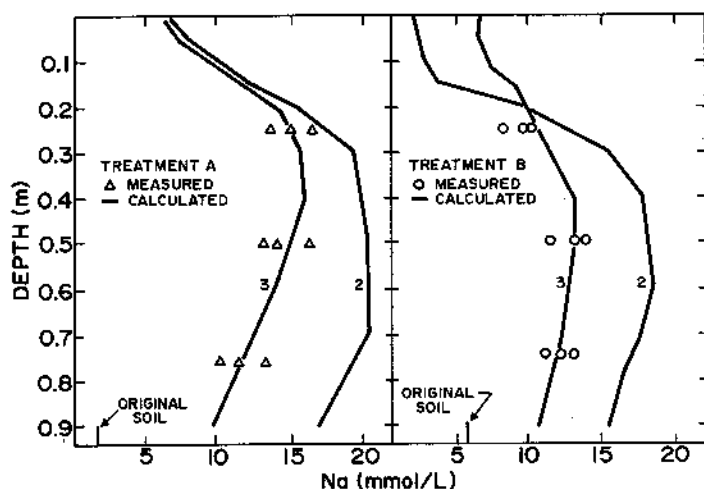
Fig. 16-4. Measured and calculated Na concentrations for Treatments A and B by solute transport and chemical precipitation (2); and solute transport, chemical precipitation, and cation exchange (3).

mix on the exchange sites. Sodium in solution, as measured and calculated, is shown in Fig. 15-4a and 15-4b for Treatments A and B, as an example. In both cases, Na was overestimated by Options 1 (data not shown) and 2, while Option 3 satisfactorily predicted Na solution concentration. Additional Na, Mg and K data are shown elsewhere (Robbins et al., 1980b).

Calcium ion concentration calculation is the most complex of the cations since it is affected by pH, CO_2 partial pressure, CO_3, HCO_3, and SO_4

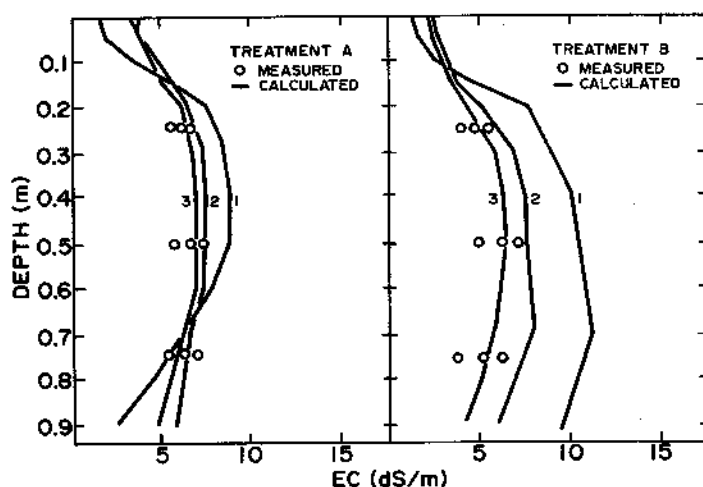Fig. 16-5. Measured and calculated Ca concentrations for Treatments A and B by solute transport only (1); solute transport and chemical precipitation (2); and solute transport, chemical precipitation, and cation exchange (3).
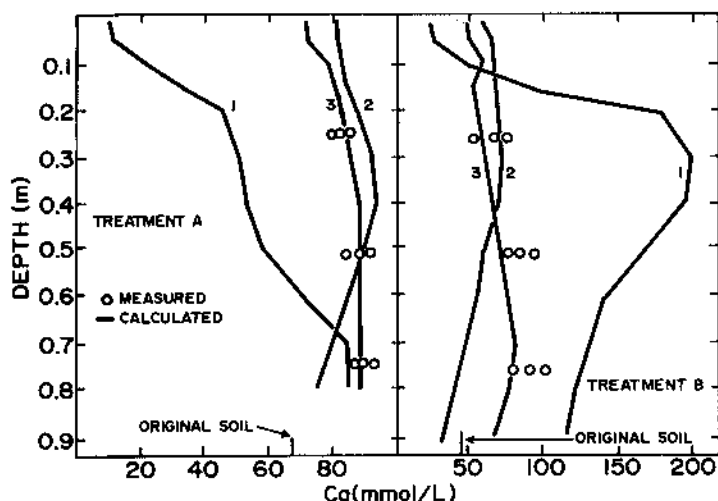
concentration through dissolution and precipitation reactions and by the other cations through exchange reactions. Consequently, Option 3 was the only calculation method that consistently predicted Ca concentration. Options 1 and 2 would either underestimate or overestimate Ca concentration depending on the concentrations of the other ions (Fig. 16-5). Since Ca concentration in solution and on the exchange sites plays such an active part in soil chemical and physical interaction, Option 3 is necessary to model these changes with time if equilibrium between the irrigation water, soil solution, and exchange phase is modeled.

In the field plot evaluation, Dudley et al. (1981) discussed Cl and Ca concentration and EC in detail. The chloride ion was selected for evaluation because it is considered to be chemically nonreactive and provides an evaluation of ion transport modeling. Calcium evaluation includes the lime and gypsum chemical reactions as well as cation exchange reactions. Overall model performance can be partially evaluated by EC prediction evaluation. Under field plot conditions, they found that Ca and Cl ion concentrations and EC values were not predicted at a given point for the short study time and conditions evaluated in the noncropped treatments. The model did not provide a method of representing the field variability found in the plots. Under cropped conditions, Ca and Cl ion concentrations and measured EC values in the field were more accurately predicted by the model than the noncropped treatments. Growing plants appeared to have an averaging effect on the measured results. This can be explained by the fact that roots of a given plant will extract water from the areas of lowest total potential (i.e., the wettest and least salty locations). Also, the wetting and drying cycles produced by the roots also will cause water to move through areas not otherwise affected by flowing water in a noncropped soil.

The original CHEM subroutine assumed a constant pH for each depth increment, and calculated CO_2 partial pressure, pH, HCO_3, and CO_3 from pH and Ca ion activity (Robbins et al., 1980a). This calculation method was used because of a lack of soil atmosphere CO_2 data for calcareous soils. Now that data are becoming available (Robbins, 1986a), it is possible to use CO_2 data as an input, and pH, HCO_3 and CO_3 can be modeled much simpler and in a more realistic manner, as is done in this version of CHEM. Because of this recent improvement, validation data are presently being obtained, but are not yet available for comparison. The calculation method and the relationships are basically the same, but CO_2 rather than pH is considered the independent variable. In the past, the $Ca-CO_3-HCO_3-CO_2$ portion of these models have been the weak section of the chemistry calculations, but with the new CO_2 data becoming available, these processes are easier to model in a more realistic manner (Robbins, 1985a, b).

VII. ADDITIONAL RESEARCH NEEDS

In addition to the reactions considered in these models, there are several additional chemical and physical reactions that are of interest under special conditions. This model supplies ion concentrations and activities necessary for additional reactions, thus leading to the systematic addition of other reactions as desired.

Many geothermal springs and wells being developed for irrigation in arid areas contain high fluoride (F) concentrations. There is concern that the F from these water sources might eventually leach into shallow water supplies used for domestic and livestock drinking water. Fluorite precipitation reactions (Tracy et al., 1984) and F adsorption in calcareous soils (Robbins, 1986b) have been sufficiently quantified so that these processes can easily be added to the CHEM subroutine for modeling high F systems.

The subroutines described here also provide the necessary soil solution electrolyte concentrations and exchangeable sodium data needed as input data for a hydraulic conductivity-infiltration rate model that could calculate changes in water flow rates caused by EC and ESP changes. Once the relationships between ESP, EC, pH, and water flow are established for a particular soil, the changes in infiltration and hydraulic conductivity rates as a function of EC and ESP changes could be added to the water flow models (Shainberg et al., 1981a). Soils with high ESPs and low to moderate ECs have been shown to differ in their responses to irrigation with very low electrolyte water or by wetting with rain water. Differences among soil minerals' tendency to release salts when exposed to low electrolyte water has been suggested to be part of the cause for differences in soil dispersion and infiltration, and hydraulic conductivity rates (Shainberg et al., 1981b).

In the past, soil-atmosphere, CO_2 partial-pressure values needed for lime equilibrium calculation have either been calculated from input pH data or, as in the case of this model, CO_2 is read in for each depth increment. In either case, the pH or CO_2 values are held constant throughout the simu-

lation. Recently, more data has become available for CO_2 concentrations and changes in calcareous soil systems (Robbins, 1986b). These data present the opportunity to develop CO_2 concentrations or CO_2 production models that would calculate CO_2 as a function of crop variety, root depth, growth stages and rates, and soil water content. Modeling CO_2 changes in the soil atmosphere could improve salinity prediction models and help increase the present knowledge of this segment of soil chemical reactions.

Under special conditions, it would also be advantageous to be able to predict the movement of such ions as boron, selenium, arsenic, and heavy metal ions. With more basic information about many of these ions, the CHEM subroutine could also be amended to predict movement of many of these ions toward the groundwater.

VIII. APPENDIX 1

PROGRAM LISTINGS

SOLUTE SUBROUTINE

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************************************************************************
      SUBROUTINE SOLUTE(K,DIFO,DIFA,DIFB,AMBDA,DD,DELT,KK,
     #SE1,SE2,SE3,SE4,SE5,SE6,SE7,SE8,SS1,SS2,SS3,SS4,SS5,SS6,SS7,SS8,
     #SSE1,SSE2,SSE3,SSE4,SSE5,SSE6,SSE7,SSE8,HEAD,IRRNO,W,Y,WF2,R9,
     #SS1,SS2,SS3,SS4,SS5,SS6,SS7,SS8)
************************************************************************
*    THIS SUBROUTINE SOLVES THE SOLUTE TRANSPORT EQUATION FOR EIGHT
*    IONS (CA,MG,NA,K,CL,SO4,HCO3,CO3 AND ARE PASSED IN AS SS1 THROUGH SS8
*    AND NEW ION CONCENTRATIONS PASSED BACK OUT AS SE1 THROUGH SE8.
*
*    DIFFUS=BRESLER'S (1973) APPARENT DIFFUSION COEFFICIENT (MM**2/DAY)
*    RHO=BULK DENSITY OF SOIL (KG/DM*3)
*    SE1 TO SE8: IONS,CURRENT TIME STEP (MMOL/L)
*
*    SSE1 TO SSE8: IONS LEACHED OUT OF ROOT ZONE (MMOL)
*    SS1 TO SS8: ION CONCENTRATIONS PREVIOUS TIME STEP (MMOL/L)
*    WF2=FLUX DENSITY OF WATER DURING CURRENT TIME STEP (MM/DAY)
*---------------------------
      DIMENSION TW(30),Y(30),W(30),WF2(30),DIFFUS(30)
      REAL DD(30),A1(30),B1(30),C1(30),D1(30),AB(30),BB(30)
      REAL CB(30),DB(30),H(30),G(30),G1(30),F1(30)
      REAL SE1(30),SE2(30),SE3(30),SE4(30),SS1(30),T(30,8),S(30,8)
      REAL SS2(30),SS3(30),SS4(30),WW(30),WW1(30)
      REAL SS5(30),SS6(30),SS7(30),SS8(30),SE5(30),SE6(30),SE7(30)
      REAL SE8(30),SF1(100),SF2(100),SF3(100)
      REAL SF4(100),SF5(100),SF6(100),SF7(100),SF8(100)
      INTEGER R9
*-------------------------
      WF21=1.
*    SET SOLUTE CONCENTRATIONS (S VALUES) TO PASSED CONCENTRATIONS
      DO 3 I=1,30
      DO 2 J=1,8
      T(I,J)=0.
```

```
      2 CONTINUE
      3 CONTINUE
        DO 5 I=2,KK
        S(I,1)=SS1(I)
        S(I,2)=SS2(I)
        S(I,3)=SS3(I)
        S(I,4)=SS4(I)
        S(I,5)=SS5(I)
        S(I,6)=SS6(I)
        S(I,7)=SS7(I)
        S(I,8)=SS8(I)
      5 CONTINUE
*---------------------
*   SET SURFACE BOUNDARY TO ZERO OR TO SOLUTE CONC. IN APPLIED
*     WATER (SF VALUES) AFTER PARTITION
        IF(HEAD.LE.0.)THEN
        DO 6 M=1,8
      6 S(1,M)=0.
        ELSE
        S(1,1)=SF1(IRRNO)
        S(1,2)=SF2(IRRNO)
        S(1,3)=SF3(IRRNO)
        S(1,4)=SF4(IRRNO)
        S(1,5)=SF5(IRRNO)
        S(1,6)=SF6(IRRNO)
        S(1,7)=SF7(IRRNO)
        S(1,8)=SF8(IRRNO)
        ENDIF
*-----------------------
*   CALC DEPTH INCREMENT (FOR EQUAL DEPTHS ONLY
        DLZ=DD(2)-DD(1)
*-----------------------
*   CALCULATE TOP AND BOTTOM WATER CONTENTS
        IF(WF2(1).LT.0.)THEN
        WF21=WF2(1)
        WF2(1)=0.
        ELSE
        W1=W(1)
        WF21=WF2(1)
        W(1)=Y(1)-WF2(1)*DELT/DLZ
        ENDIF
        IF(R9.EQ.3)WF2(KK-1)=0.
*-----------------------
*   MEAN THETA; DIFFUSION COEFFICIENT; PORE WATER VELOCITY BETWEEN
*   NODES; PORE WATER VELOCITY ACROSS NODES
        DO 10 I=1,KK-1
        TW(I)=(Y(I+1)+W(I+1)+Y(I)+W(I))/4.
        DIFFUS(I)=DIFO*DIFA*EXP(DIFB*TW(I))+AMBDA*ABS(WF2(I)/TW(I))
        IF(I.EQ.1.AND.WF2(1).EQ.0.)DIFFUS(I)=0.
        WW1(I)=WF2(I)/TW(I)
        IF(I.GT.1)WW(I)=((WF2(I-1)+WF2(I))/2.)/((W(I)+Y(I))/2.)
     10 CONTINUE
*-----------------------
*   CONSTANTS FOR THE DIFFUSION/CONVECTION EQUATION
        DO 20 I=2,KK-1
        AB(I)=(DIFFUS(I-1)-DLZ*WF2(I-1)/2.-WW(I)*WW1(I-1)*DELT*
       *(W(I-1)-Y(I-1))/8.)/(2.*DLZ*DLZ)
        BB(I)=(DIFFUS(I)-DLZ*WF2(I)/2.-WW(I)*WW1(I)*DELT*
       *(W(I)-Y(I))/8.)/(2.*DLZ*DLZ)
        DB(I)=WF2(I)/(2.*DLZ)
        CB(I)=WF2(I-1)/(2.*DLZ)
```

```
      20 CONTINUE
*------------------------------
*   DIFFUSION TERMS IGNORED IN BOUNDARY SEGMENTS
          AB(2)=0.
          BB(KK-1)=0.
*------------------------------
          DO 25 M=1,8
          DO 30 I=2,K
*   SET BETA VALUES TO 0 OR 1 ACCORDING TO DIRECTION OF WATER FLOW
          IF(WF2(I).GT.0.)THEN
          BETA2=1.
          BETA3=0.
          ELSE
          BETA2=0.
          BETA3=1.
          ENDIF
          IF(WF2(I-1).GT.0.)THEN
          BETA1=1.
          BETA4=0.
          ELSE
          BETA1=0.
          BETA4=1.
          ENDIF
*------------------------------
*   COEFFICIENTS FOR TRIDIAGONAL MATRIX
          A1(I)=-AB(I)-BETA1*CB(I)
          B1(I)=W(I)/DELT+AB(I)+BB(I)+BETA2*DB(I)-BETA4*CB(I)
          C1(I)=-BB(I)+BETA3*DB(I)
          D1(I)=S(I-1,M)*(AB(I)+BETA1*CB(I))
          #+S(I,M)*(Y(I)/DELT-AB(I)-BETA2*DB(I)
          #+BETA4*CB(I)-BB(I))
          #+S(I+1,M)*(BB(I)-BETA3*DB(I))
      30 CONTINUE
*------------------------------
*   SOLVING TRIDIAGONAL MATRIX
*   I) CALC. F & G COEFFICIENTS FROM NODES 2 TO K
          F1(2)=C1(2)/B1(2)
          G1(2)=(D1(2)-A1(2)*S(1,M))/B1(2)
          DO 40 J=3,K
          F1(J)=C1(J)/(B1(J)-F1(J-1)*A1(J))
      40 G1(J)=(D1(J)-A1(J)*G1(J-1))/(B1(J)-A1(J)*F1(J-1))
*----
*   SET BOTTOM BOUNDARY CONDITION
*   I)WATER TABLE OF CONSTANT CONCENTRATION
          IF(R9.EQ.1)T(KK,M)=S(KK,M)
*   II) UNIT HYDRAULIC GRADIENT
          IF(R9.EQ.2)T(KK,M)=S(KK,M)
*   III) ZERO FLUX (DEPENDS ON WHETHER SALT IS ADDED OR LOST)
          IF(R9.EQ.3)T(KK,M)=0.
*----
*   NEW SOLUTE CONCENTRATIONS : T(I,M) VALUES
          J=KK
      50 J=J-1
          T(J,M)=G1(J)-F1(J)*T(J+1,M)
          IF(J.GT.2)GO TO 50
      25 CONTINUE
*------------------------------
*   ADJUST BOUNDARY VALUES BACK TO ORIGINAL WATER CONTENTS AND FLUXES
          IF(WF21.LE.0.)THEN
          WF2(1)=WF21
          ENDIF
```

```
*-----------------------
*---------------------
*   CALCULATE DRAINAGE AS FLUX * CONC. FROM SEGMENT K
        SSE1=SSE1+WF2(K)*DELT*(S(K,1)+T(K,1))/2.
        SSE2=SSE2+WF2(K)*DELT*(S(K,2)+T(K,2))/2.
        SSE3=SSE3+WF2(K)*DELT*(S(K,3)+T(K,3))/2.
        SSE4=SSE4+WF2(K)*DELT*(S(K,4)+T(K,4))/2.
        SSE5=SSE5+WF2(K)*DELT*(S(K,5)+T(K,5))/2.
        SSE6=SSE6+WF2(K)*DELT*(S(K,6)+T(K,6))/2.
        SSE7=SSE7+WF2(K)*DELT*(S(K,7)+T(K,7))/2.
        SSE8=SSE8+WF2(K)*DELT*(S(K,8)+T(K,8))/2.
*-----------------------
*   SET PASSED SE VALUES TO NEW SOLUTE CONCENTRATIONS
        DO 60 I=2,KK
        SE1(I)=T(I,1)
        SE2(I)=T(I,2)
        SE3(I)=T(I,3)
        SE4(I)=T(I,4)
        SE5(I)=T(I,5)
        SE6(I)=T(I,6)
        SE7(I)=T(I,7)
        SE8(I)=T(I,8)
        IF(SE1(I).LT.1.0E-15)SE1(I)=0.0
        IF(SE2(I).LT.1.0E-15)SE2(I)=0.0
        IF(SE3(I).LT.1.0E-15)SE3(I)=0.0
        IF(SE4(I).LT.1.0E-15)SE4(I)=0.0
        IF(SE5(I).LT.1.0E-15)SE5(I)=0.0
        IF(SE6(I).LT.1.0E-15)SE6(I)=0.0
        IF(SE7(I).LT.1.0E-15)SE7(I)=0.0
        IF(SE8(I).LT.1.0E-15)SE8(I)=0.0
    60 CONTINUE
*-----------------------
        RETURN
        END
***********************************************************
```

CHEM SUBROUTINE

```
***********************************************************************
        SUBROUTINE CHEM(CACO,CASO,PCO2,BD,TCA,TMG,TNA,TK,TCL,TSO4,
    #THCO3,TCO3,VH2O,EC,SAR,XCA,XMG,XNA,XK,CEC,ESP,NN,K1,K2,K3,K4,K5,
    #K6,PH,DELGYP,DELIME)
***********************************************************************
*
*   THE CHEM SUBROUTINE AND THE FIVE DEPENDENT SUBROUTINES ARE INTENDED
*   TO BE USED TOGETHER AND INTERFACED WITH EXISTING STEADY STATE
*   OR TRANSIENT WATER FLOW, SALT TRANSPORT MODELS.  FOR USE WITH STEADY
*   STATE MODELS THE FIRST SECTION OF XCHANG IS USED (NN=1)
*   THESE SUBROUTINES ARE INTENDED TO PROVIDE A MORE THERMODYNAMICALLY
*   RIGOROUS DESCRIPTION OF LIME AND GYPSUM PRECIPITATION AND DISSOL-
*   UTION AND CATION EXCHANGE EQUILIBRIUM IN MINERAL SOILS CONTAINING
*   LIME WITH MEDIUM TO HIGH SALT CONCENTRATIONS.  THIS SUBROUTINE ALSO
*   ASSUMES THAT pH OF EACH INCREMENT CONTROLLED BY CO2 PARTIAL PRESSURE
*
*   REQUIRED DATA IN ORDER OF LISTING IN THE CALLING STATEMENT ARE:
*   CASO=GYPSUM  CACO=LIME   (DECIMAL FRACTION ON WT. BASIS)
*   PCO2=CARBON DIOXIDE PARTIAL PRESSURE (PERCENT CO2 OR kPa)
*   BD=SOIL BULK DENSITY (G/CUBIC CM.)
```

```
*    TCA=CALCIUM        TMG=MAGNESIUM       TNA=SODIUM
*    TK=POTASSIUM       TCL=CHLORIDE        TSO4=SULFATE
*              (MMOL/L IN SOLUTION)
*    VH2O=VOLUMETRIC WATER CONTENT FOR DEPTH INCREMENT.
*    CEC=CATION EXCHANGE CAPACITY (MEQ/100G OR MEQ/KG OR MOLES OF CHARGE/
*    KG). IF CEC=0 THEN XCHANG IS NOT CALLED.
*    IF XCHANG IS CALLED AND NN IS NOT EQUAL TO 1, VALUES ARE NEEDED FOR
*    THE CATION EXCHANGE SELECTIVITY COEFFICIENTS K1, K2,....K6 THESE ARE
*    USED TO CALCULATE STARTING VALUES FOR THE EXCHANGEABLE CATIONS, XCA
*    XMG XNA AND XK (UNITS ARE SAME AS CEC). IF NN NOT=1 INPUT VALUES FOR
*    XCA, XMG, XNA AND XK ARE NEEDED. FOR ALL CASES WHERE CEC NOT EQUAL
*    TO ZERO, NEW VALUES ARE CALCULATED FOR XCA XMG XNA AND XK. AND
*    PASSED BACK TO THE CALLING PROGRAM. AFTER EXECUTION THE CHEM
*    SUBROUTINE ALSO RETURNS NEW VALUES FOR ALL LISTED VARIABLES EXCEPT
*    PCO2, BD, VH2O, CEC, K1, K2, K3, K4, K5, AND K6,
*    THE OTHER OUT PUT VARIABLES ARE:
*    THCO3=BICARBONATE      TCO3=CARBONATE      (MMOLE/L)
*    EC=ELECTRICAL CONDUCTIVITY  (MMHOS/CM OR dS/M)
*    SAR=SODIUM ABSORBTION RATIO
*    ESP=EXCHANGEABLE SODIUM PERCENTAGE
*    DELGYP=CHANGE IN GYPSUM DURING EXECUTION STEP
*    DELIME=CHANGE IN LIME DURING EXECUTION STEP
*
*    OTHER FORTRAN SYMBOLS USED IN THE SUBROUTINE.
*    CHEMICAL CONSTANTS USED IN THE DATA STATEMENT;
*    KH  HENRYS LAW CONSTANT FOR CO2
*    KW  STABILITY CONSTANT FOR WATER
*    KA1 FIRST DISSOCIATION CONSTANT FOR H2CO3
*    KA2 SECOND DISSOCIATION CONSTANT FOR H2CO3
*    KD1 STABILITY CONSTANT OF CACO3
*    KD2 STABILITY CONSTANT OF CAHCO3+
*    KD3 STABILITY CONSTANT OF CAOH+
*    KD4 STABILITY CONSTANT OF CASO4
*    KD5 STABILITY CONSTANT OF MGCO3
*    KD6 STABILITY CONSTANT OF MGHCO3+
*    KD7 STABILITY CONSTANT OF MGOH+
*    KD8 STABILITY CONSTANT OF MGSO4
*    KD9 STABILITY CONSTANT OF NASO4-
*    KD10 STABILITY CONSTANT OF NACO3-
*    SP1 SOLUBILITY PRODUCT OF GYPSUM
*    SP2 SOLUBILITY PRODUCT OF LIME
*    H=HYDROGEN ION ACTIVITY  (MOLES/L)
*    ADJGYP AND ADJLIME CONVERT GYPSUM AND LIME BETWEEN
*    DECIMAL FRACTIONS AND MOLES/L IN SOLUTION.
*    ACT1 AND ACT2 ARE THE ACTIVITY COEFFICIENTS FOR MONO- AND
*    DIVALENT IONS
*    CHEMICAL SYMBOLS PRECEDED BY A, REPRESENT ION ACTIVITIES-
*    (ACA=CALCIUM ACTIVITY ETC.).

*    ACCA IS THE "APPARENT" ACTIVITY COEFFICIENT OF CALCIUM.
*    CAT AND AN ARE THE SUM OF CATIONS AND ANIONS (EQUIV./L).
*
     REAL KH,KW,KA1,KA2,KD1,KD2,KD3,KD4,KD5,KD6,KD7,KD8,KD9,
#KD10
     REAL K1,K2,K3,K4,K5,K6
     DATA KH/.0339/,KW/.1E-13/,KA1/.5E-6/,KA2/.5E-10/,KD1/.63E-3/,
#KD2/.055/,KD3/.0425/,KD4/.49E-2/,KD5/.4E-3/,KD6/.069/,
#KD7/.263E-2/,KD8/.0063/,KD9/.24/,KD10/.0535/,SP1/.24E-4/,
#SP2/.113E-7/
*
```

```
*    CONCENTRATIONS ARE CONVERTED FROM MMOL/L TO MOLES/L AND
*    APPROXIMATE VALUES ARE GIVEN TO THCO3 AND TCO3.
*
     TCA=TCA/1000.
     TMG=TMG/1000.
     TNA=TNA/1000.
     TK=TK/1000.
     TCL=TCL/1000.
     TSO4=TSO4/1000.
     THCO3=2.0*(TCA+TMG-TSO4)+TNA+TK-TCL
     IF (THCO3.LT.0.0) THCO3=0.0
     TCO3=0.0
*
*    CO2 PARTIAL PRESSURE CONVERTED TO ATMOSPHERES.
*
     PCO2=PCO2/100.
*
*    LIME AND GYPSUM ARE CONVERTED FROM DECIMAL FRACTIONS ON A WEIGHT
*    BASIS TO MOLES/L SOIL SOLUTION.
*
     ADJGYP=BD*5.81/VH2O
     CASO=CASO*ADJGYP
     CASOIN=CASO
     ADJLIM=BD*10./VH2O

     CACO=CACO*ADJLIM
*    STARTING VALUES OF LIME AND GYPSUM RECORDED SO THAT PRECIPITATION
*    AND DISSOLUTION CAN BE CALCULATED
     ALIME=CACO
     AGYP=CASO
*
*    EC IS CALCULATED FROM IONIC CONCENTRATIONS AND USED TO CALCULATE
*    THE MONO- AND DIVALENT ION ACTIVITY COEFFICIENTS.
*
     CALL ECM3(TCA,TMG,TNA,TK,TCL,TSO4,THCO3,TCO3,EC)
     ACT1=ACT(1.,EC)
     ACT2=ACT(2.,EC)
*
*    FIRST APPROXIMATIONS OF ION ACTIVITY ARE MADE FROM ACTIVITY
*    COEFFICIENTS AND THE ION PAIRS THAT CAN BE CONSIDERED AT THIS
*    POINT.
*
     ASO4=TSO4*ACT2
     AK=TK*ACT1
     ANA=TNA*ACT1/(1.0+ASO4/KD9)
     ACA=TCA/(1./ACT2+KW/(KD3*ACT1*H)+ASO4/KD4)
     AMG=TMG/(1./ACT2+KW/(KD7*ACT1*H)+ASO4/KD8)
     ASO4=TSO4/(1./ACT2+ACA/KD4+AMG/KD8+ANA/(ACT1*KD9))
     H=SQRT(PCO2*KH*KA1*KA2*ACA/SP2)
*

*    CHEMICAL EQUILIBRIUM LOOP
*
     DO 20 I=1,5
*
*    NEW ACTIVITY COEFFICIENTS ARE CALCULATED FROM THE EC VALUE
*    FROM THE PREVIOUS CYCLE AND A NEW PCO2 VALUE IS CALCULATED.
*
     ACT1=ACT(1.,EC)
     ACT2=ACT(2.,EC)
```

```
*
*    ACTIVITIES FOR CA, MG, NA, SO4, ARE CORRECTED FOR IONIC
*    STRENGTH AND ION PAIRING, AND ACO3 IS CALCULATED.
*
      ACA=TCA/(1./ACT2+KA1*KH*PCO2/(KD2*ACT1*H)+KW/(KD3*ACT1*H)+
     #KA1*KA2*KH*PCO2/(KD1*H*H)+ASO4/KD4)
      AMG=TMG/(1./ACT2+KA1*KH*PCO2/(KD6*ACT1*H)+KW/(KD7*ACT1*H)+
     *KA1*KA2*KH*PCO2/(KD5*H*H)+ASO4/KD8)
      ANA=TNA/(1./ACT1+ASO4/(ACT1*KD9)+KA1*KA2*KH*PCO2/(KD10*ACT2*H*H))
      ASO4=TSO4/(1./ACT2+ACA/KD4+AMG/KD8+ANA/(ACT1*KD9))
      H=SQRT(PCO2*KH*KA1*KA2*ACA/SP2)
      ACO3=KA1*KA2*KH*PCO2/(H*H)
*
*    THE SOIL SOLUTION IS EQUILIBRATED WITH LIME AND GYPSUM.
*
      CALL PRECIP(ACA,ACO3,ASO4,TCA,TSO4,CACO,CASO)
*
      ACA=TCA/(1./ACT2+KA1*KH*PCO2/(KD2*ACT1*H)+KW/(KD3*ACT1*H)+
     *KA1*KA2*KH*PCO2/(KD1*H*H)+ASO4/KD4)
      EQUIV=2.*(TCA+TMG-TSO4)+TNA+TK-TCL
      THCO3=H*EQUIV/(KA2*2.+H)
      TCO3=(EQUIV-THCO3)/2.0
      ECOLD=EC
      CALL ECM3(TCA,TMG,TNA,TK,TCL,TSO4,THCO3,TCO3,EC)
      IF(ABS(EC-ECOLD).LT.EC*0.01)GO TO 22
  20  CONTINUE
  22  PH=-ALOG10(H)
*
  40  IF(CEC.EQ.0.)GOTO 45
      CALL XCHANG(TCA,TMG,TNA,TK,ACA,AMG,ANA,AK,XCA,XMG,XNA,XK,
     *BD,VH2O,CEC,NN,K1,K2,K3,K4,K5,K6)
*
*    MOLES/L IN SOLUTION ARE CONVERTED TO MMOL/L AND GYPSUM AND LIME
*    ARE CONVERTED BACK TO DECIMAL FRACTIONS.  SAR IS ALSO CALCULATED.
*
  45  TCA=TCA*1000.
      TMG=TMG*1000.
      TNA=TNA*1000.
      TK=TK*1000.
      TSO4=TSO4*1000.
      THCO3=THCO3*1000.
      TCO3=TCO3*1000.
      TCL=TCL*1000.
C PRECIPITATION OR DISSOLUTION OF LIME AND GYPSUM DURING TIME STEP
      DELGYP=(CASO-AGYP)*1000.
      DELIME=(CACO-ALIME)*1000.
      CASO=CASO/ADJGYP
      CACO=CACO/ADJLIM
      SAR=TNA/SQRT(TCA+TMG)
      ESP=XNA*100./CEC
*
*    CO2 PARTIAL PRESSURE CONVERTED BACK TO PERCENT OR kPa.
*
      PCO2=PCO2*100.
  60  CONTINUE
      RETURN
      END
************************************************************************
```

FUNCTION ACT

****

```
*    THE FUNCTION ACT CALCULATES IONIC STRENGTH (IS) USING THE
*    APPROXIMATION OF GRIFFIN AND JURINAK (1973). THE SQUARE ROOT
*    (I) OF (IS) IS THEN USED IN THE DAVIES EQUATION TO CALCULATE
*    THE MONO- (Z=1) AND DIVALENT (Z=2) ION MEAN ACTIVITY COEFFICIENTS.
*
     FUNCTION ACT(Z,EC)
     REAL IS,I
     IS=0.0127*EC
     I=SQRT(IS)
     ACT=10.0**(-0.509*Z*Z*(I/(1.0+I)-0.3*IS))
     RETURN
     END
```
****

PRECIP SUBROUTINE

****

```
*    THE SUBROUTINE PRECIP USES CATION (CAT) AND ANION (AN) ACTIVITIES
*    AND THE SOLUBILITY PRODUCT (SP) TO DETERMINE IF SOLID PHASE
*    MATERIAL (PPT) MUST DISSOLVE OR PRECIPITATE TO BRING THE SYSTEM
*    INTO CHEMICAL EQUILIBRIUM. IT THEN CALLS THE SINK SUBROUTINE TO
*    DETERMINE THE QUANTITY OF PPT TO BE DISSOLVED OR PRECIPITATED.
*    XX AND YY ARE THE SINK SUBROUTINE STARTING VALUE ON INPUT, AND COME
*    BACK FROM SINK AS THE VALUE THAT CAT, AN AND PPT IS TO BE CHANGED.
*
     SUBROUTINE PRECIP(ACA,ACO3,ASO4,TCA,TSO4,CACO,CASO)
     DATA SP1/.24E-04/,SP2/.113E-07/
     ACCA=ACA/TCA
     ACSO=ASO4/TSO4
     YY=SP1
     XX=SP2
*
*    IF THE SOIL INCREMENT CONTAINS GYPSUM AND IS UNDERSATURATED WITH
*    RESPECT TO GYPSUM, GOTO 30.
*
     IF(ACA*ASO4.LT.SP1.AND.CASO.GT.0.0)GO TO 30
*
*    IF THE INCREMENT IS SUPERSATURATED WITH GYPSUM, GOTO 40
*
     IF(ACA*ASO4.GT.SP1)GO TO 40
*
*    IF THE INCREMENT IS UNDERSATURATED WITH LIME, GOTO 10, OF IF IN
*    EQUILIBRIUM WITH LIME GOTO 50, OR IF SUPERSATURATED WITH LIME GOTO
*    20
*
   5 IF(ACA*ACO3-SP2)10,50,20
  10 CALL SINK(ACA,ACO3,SP2,XX)
     CACO=CACO-XX/ACCA
     TCA=TCA+XX/ACCA
     ACA=ACA+XX
     GO TO 50
  20 CALL SINK(ACA,ACO3,SP2,XX)
     CACO=CACO+XX/ACCA
     TCA=TCA-XX/ACCA
```

```
        ACA=ACA+XX
        GO TO 50
 30     CALL SINK(ACA,ASO4,SP1,YY)
        IF((YY/ACSO).GT.CASO)YY=CASO*ACSO
        CASO=CASO-YY/ACSO
        TCA=TCA+YY/ACSO
        ACA=ACA+YY
        TSO4=TSO4+YY/ACSO
        ASO4=ASO4+YY
*
*   GOTO 5 TO CHECK LIME EQUILIBRIUM.
*
        GO TO 5
 40     CALL SINK(ACA,ASO4,SP1,YY)
        CASO=CASO+YY/ACSO
        TCA=TCA-YY/ACSO
        ACA=ACA-ACSO
        TSO4=TSO4-YY/ACSO
        ASO4=ASO4-YY
*
*   GOTO 5 TO CHECK LIME EQUILIBRIUM.
*
        GO TO 5
 50     CONTINUE
        RETURN
        END
***********************************************************************
```

SINK SUBROUTINE

```
***********************************************************************
*    THE SUBROUTINE SINK USES CATION (CAT) AND ANION (AN) ACTIVITIES,
*    SOLUBILITY PRODUCT (SP), AND A STARTING VALUE (X) TO CALCULATE THE
*    CATION AND ANION ACTIVITY CHANGE DUE TO SOLUTION OR PRECIPITATION
*    OF SOLID PHASE TO BRING THE SYSTEM INTO CHEMICAL EQUILIBRIUM FOR
*    A GIVEN SPECIES. THE NEWTON METHOD IS USED TO FIND X.
*
        SUBROUTINE SINK(CAT,AN,SP,X)
        DO 5 N=1,10
*
*    THIS STATEMENT KEEPS THE NEXT FROM DIVIDING BY ZERO
*
        IF(CAT+AN.EQ.2.0*X)X=X*1.1
        XI=X-(X*X-X*CAT-X*AN+CAT*AN-SP)/(2.0*X-CAT-AN)
        IF(ABS(XI-X).LT.ABS(XI*.01)) GOTO 10
        X=XI
 5      CONTINUE
 10     X=ABS(X)
        RETURN
        END
***********************************************************************
```

XCHANG SUBROUTINE

```
***********************************************************************
*    THE SUBROUTINE XCHANG IS DIVIDED INTO TWO SEGMENTS. IF NN EQUALS
*    1, INITIAL EXCHANGEABLE CATION CONCENTRATIONS ARE CALCULATED FROM
*    THE CATION EXCHANGE CAPACITY (CEC), AND CATION ACTIVITIES SUPPLIED
```

```
*    BY THE CALLING PROGRAM. IF NN IS NOT EQUAL TO 1, NEW EQUILIBRIUM
*    IS CALCULATED FOR SOLUTION AND EXCHANGEABLE CATIONS USING
*    EXCHANGEABLE CATION AND SOLUTION CATION CONCENTRATIONS AND CATION
*    ACTIVITIES, BULK DENSITY (BD), VOLUMETRIC WATER CONTENT (VH2O),
*    AND CEC VALUES SUPPLIED FROM THE CALLING PROGRAM.
*    TCA, TMG,...ETC ARE MOLES/L OF SOLUTION CATIONS
*    ACA, AMG,...ETC ARE CATION ACTIVITIES
*    XCA,XMG,...ETC ARE EXCHANGEABLE CATIONS, INITIALLY AND FINALLY IN
*    MEQ/100G OF SOIL AND WITHIN THE SUBROUTINE THEY ARE CONVERTED TO
*    AND FROM MOLES/L.
*    OTHER FORTRAN SYMBOLS ARE SELF EXPLANATORY.
*
         SUBROUTINE XCHANG(TCA,TMG,TNA,TK,ACA,AMG,ANA,AK,XCA,XMG,XNA,XK,
        *BD,VH2O,CEC,NN,K1,K2,K3,K4,K5,K6)
*
*    SOME OF THE SELECTIVITY COEFFICIENTS, K1,K2,K3, ETC MAY VARY FROM
*    SOIL TO SOIL.
*
         REAL K1,K2,K3,K4,K5,K6
         IF(NN.EQ.1)GOTO 10
         GOTO 20
*
*    STARTING POINT EXCHANGEABLE CATION VALUES ARE CALCULATED FROM
*    INITIAL INPUT DATA OR EXCHANGEABLE CATIONS ARE CALCULATED FOR STEADY
*    STATE CALCULATIONS.
*
*    STARTING POINT EXCHANGEABLE CATION VALUES ARE CALCULATED FROM
*    INITIAL INPUT DATA OR EXCHANGEABLE CATIONS ARE CALCULATED FOR STEADY
*    STATE CALCULATIONS.
*
   10    ZCA=SQRT(ACA)
         ZMG=SQRT(AMG)
         XCA=CEC/(ZMG/(K1*ZCA)+ANA/(ZCA*K2)+AK*K3/ZCA+1.)
         XMG=CEC/(ZCA*K1/ZMG+ANA/(ZMG*K5)+AK*K4/ZMG+1.)
         XNA=CEC/(ZCA*K2/ANA+ZMG*K5/ANA+AK*K6/ANA+1.)
         XK=CEC/(ZCA/(K3*AK)+ZMG/(K4*AK)+ANA/(AK*K6)+1.)
*
*    THE EXCHANGEABLE CATIONS ARE CORRECTED BY A COMMON FACTOR TO FORCE
*    THE SUM OF EXCHANGEABLE CATIONS TO EQUAL THE CEC.  IN A FEW CASES
*    MACHINE ROUND-OFF ERROR MAKES THIS NECESSARY.
*
         C=CEC/(XCA+XMG+XNA+XK)
         XCA=XCA*C
         XMG=XMG*C
         XNA=XNA*C
         XK=XK*C
         NN=1
         GOTO 50
*
*    ADJUSTMENT FACTORS ARE CALCULATED TO CONVERT EXCHANGEABLE CATION
*    UNITS BETWEEN MEQ/100G OF SOIL AND MOLES/L IN SOLUTION.
*                   !!!! WARNING !!!!
*    IF EXCHANGEABLE CATION UNITS ARE MEQ/KG OF SOIL OR MMOLES OF CHARGE
*    PER KG THEN:
* 20  ADJ2=0.0005
*     ADJ1=0.0010
*    OTHERWISE:
*
   20    ADJ2=0.005*BD/VH2O
```

```
        ADJ1=0.010*BD/VH2O
        XCA=XCA*ADJ2
        XMG=XMG*ADJ2
        XNA=XNA*ADJ1
        XK=XK*ADJ1
        EQU=2.*(TCA+TMG)+TNA+TK
*
*    "APPARENT ACTIVITY COEFFICIENTS" ARE CALCULATED FOR EACH CATION.
*
        ACCA=ACA/TCA
        ACMG=AMG/TMG
        ACNA=ANA/TNA
        ACK=AK/TK
*
*    THE SUM OF EACH SOLUTION PLUS EXCHANGEABLE CATION IS CALCULATED.
*
        SCA=TCA+XCA
        SMG=TMG+XMG
        SNA=TNA+XNA
        SK=TK+XK
*
*    THIS LOOP BRINGS THE NEW EXCHANGEABLE AND SOLUTION CATIONS INTO EQUI-
*    LIBRIUM WITH EACH OTHER, ASSUMING, (1)THAT THE APPARENT ACTIVITY
*    COEFFICIENTS ARE CONSTANT, (2) THAT THE CEC IS CONSTANT AND EQUAL
*    TO THE SUM OF THE EXCHANGEABLE CATIONS, AND (3) THAT EACH EXCHANGE-
*    ABLE PLUS SOLUTION CATION CONCENTRATION REMAINS CONSTANT.
*
        DO 30 I=1,4
        ZCA=SQRT(ACA)
        ZMG=SQRT(AMG)
        XCANU=CEC/(ZMG/(K1*ZCA)+ANA/(ZCA*K2)+AK*K3/ZCA+1.)
        XMGNU=CEC/(ZCA*K1/ZMG+ANA/(ZMG*K5)+AK*K4/ZMG+1.)
        XNANU=CEC/(ZCA*K2/ANA+ZMG*K5/ANA+AK*K6/ANA+1.)
        XXNU=CEC/(ZCA/(K3*AK)+ZMG/(K4*AK)+ANA/(AK*K6)+1.)
        XCANU=XCANU*ADJ2
        XMGNU=XMGNU*ADJ2
        XNANU=XNANU*ADJ1
        XKNU=XKNU*ADJ1
        TCA=TCA*XCA*2./(XCANU+XCA)
        TMG=TMG*XMG*2./(XMGNU+XMG)
        TNA=TNA*XNA*2./(XNANU+XNA)
        TK=TK*XK*2./(XKNU+XK)
        EQUNU=2.*(TCA+TMG)+TNA+TK
        CC=EQU/EQUNU
        TCA=TCA*CC
        TMG=TMG*CC
        TNA=TNA*CC
        TK=TK*CC
        XCA=SCA-TCA
        XMG=SMG-TMG
        XNA=SNA-TNA
        XK=SK-TK
        C=CEC/((XCA+XMG)/ADJ2+(XNA+XK)/ADJ1)
        XCA=XCA*C
        XMG=XMG*C
        XNA=XNA*C
        XK=XK*C
        ACA=TCA*ACCA
        AMG=TMG*ACMG
        ANA=TNA*ACNA
        AK=TK*ACK
```

```
   30 CONTINUE
      XCA=XCA/ADJ2
      XMG=XMG/ADJ2
      XNA=XNA/ADJ1
      XK=XK/ADJ1
   50 RETURN
      END
```
****

ECM3 SUBROUTINE

****
****ELECTRICAL CONDUCTIVITY SUBROUTINE USING THE METHOD OF MCNEAL et al.
* 1970. SOIL SCI. 110:405-414. CONCENTRATION UNITS FOR INPUT IONS MUST
* BE MOLES/L. IF MEQ/L ARE USED THEN X AND Y EQUAL 1.0.
*

```
      SUBROUTINE ECM3(TCA,TMG,TNA,TK,TCL,TSO4,THCO3,TCO3,EC)
      REAL MG
      X=1000.
      Y=2000.
      CA=TCA
      MG=TMG
      SO4=TSO4
      IF(SO4.GT.CA)GOTO 10
      CASO=SO4
      CA=CA-SO4
      SO4=0.
      GOTO 30
   10 CASO=CA
      SO4=SO4-CA
      CA=0.
      IF(SO4.GT.MG)GOTO 20
      CASO=CASO+SO4
      MG=MG-SO4
      SO4=0.
      GOTO 30
   20 CASO=CASO+MG
      SO4=SO4-MG
      MG=0.
   30 EC=.05641*((CA*Y)**.9202)+.05099*((MG*Y)**.9102)+.04748*((TNA*X)
     #**.9495)+.07263*((TK*X)**.9706)+.069*((SO4*Y)**.8973)+.0733*((
     #TCO3*Y)**.8719)+.04143*((THCO3*X)**.9501)+.07206*((TCL*X)**.9671
     #)+.1133*((CASO*Y)**.8463)
      RETURN
      END
      END$
```
****

EXCHANGE COEFFICIENT PROGRAM


```
FTN7X
$FILES 0,2
      PROGRAM XCOEF
*
*     THIS PROGRAM USES SOIL SOLUTION ION CONCENTRATIONS(UNITS=meq/L)
*     EXCHANGEABLE ION CONCENTRATIONS(UNITS=meq/100g, meq/Kg or mmoles
*     OF CHARGE/Kg OF SOIL), PH AND CEC(UNITS SAME AS EXCH. IONS) TO
```

```
*     CALCULATE CATION EXCHANGE COEFFICIENTS NEEDED FOR OTHER CATION
*     EXCHANGE MODELS. THE METHODS USED FOR THESE CALCULATIONS ARE
*     DESCRIBED BY ROBBINS AND CARTER (1983 IRRIGATION SCIENCE 4:95-102.)
*     THESE VALUES SHOULD NOT BE USED IN MODELS OF ROBBINS et al. WRITTEN
*     PRIOR TO OCT 1985 WITHOUT CHANGING THE EQUATIONS USED TO CALCULATE
*     EXCHANGEABLE CATIONS UNLESS THE RECIPROCAL VALUES FOR K1, K3 AND
*     K4 ARE USED.
*
      CHARACTER*32 INPUT,OUTPUT
      CHARACTER*10 SAMPLE
      REAL KH,KW,KA1,KA2,KD1,KD2,KD3,KD4,KD5,KD6,KD7,KD8,KD9,KD10
      REAL K1,K2,K3,K4,K5,K6
      DATA KH/.0339/,KW/.1E-13/,KA1/.5E-6/,KA2/.5E-10/,KD1/.63E-3/,KD2/.
#055/,KD3/.0425/,KD4/.0049/,KD5/.0004/,KD6/.069/,KD7/.0026/,KD8/.00
    #63/,KD9/.24/,KD10/.054/,SP1/.24E-4/,SP2/.113E-7/
      WRITE(1,'("WHAT IS THE INPUT FILE NAME.")')
      READ(1,'(A32)')INPUT
      WRITE(1,'("WHAT IS THE OUTPUT FILE NAME")')
      READ(1,'(A32)')OUTPUT
      OPEN(10,FILE=INPUT,STATUS='OLD',IOSTAT=IER)
      if(ier.ne.0) write(1,'("error on open1",i5)')ier
      OPEN(16,FILE=OUTPUT,STATUS='NEW',IOSTAT=IER)
      if(ier.ne.0) write(1,'("error on open2",i5)')ier
      READ(10,100)
100   FORMAT(//)
      READ(10,102)NN
102   FORMAT(30X,I5)
      READ(10,100)
      WRITE(16,60)
60    FORMAT(" CATION EXCHANGE SELECTIVITY COEFFICIENTS CALCULATED ")
      WRITE(16,61)
61    FORMAT(" AS DESCRIBED BY ROBBINS & CARTER, 1983 IRRIGATION SCIENCE
      #")
      WRITE(16,100)
      WRITE(16,62)
62    FORMAT("              K1    K2    K3    K4    K5    K6"
      # )
      WRITE(16,63)
63    FORMAT(" SAMPLE   (CA/MG) (CA/NA) (K/CA) (K/MG) (MG/NA) (K/NA
      #)  ")
      DO 50 I=1,NN
      READ(10,104)SAMPLE,TCA,TMG,TNA,TK,TCL,TSO4,THCO3,TCO3,XCA,XMG,XNA
      #,XK,PH,CEC
104   FORMAT(A10,14F5.2)
      Z1=1000.
      Z2=2000.
      TCA=TCA/Z2
      TMG=TMG/Z2
      TNA=TNA/Z1
      TK=TK/Z1
      TCL=TCL/Z1
      TSO4=TSO4/Z2
      THCO3=THCO3/Z1
      TCO3=TCO3/Z2
      IF(PH.LT.5.)GOTO 1
      GOTO 2
1     WRITE(16,51)
      GOTO 50
2     IF(TCA.LE.0.OR.TMG.LE.0.OR.TNA.LE.0.OR.TK.LE.0.OR.TCL.LE.0.OR.TSO4
      #.LE.0.)GOTO 3
```

```
          GOTO 4
    3     WRITE(16,52)
          GOTO 50
    4     IF(CEC.NE.(XCA+XMG+XNA+XK))CEC=XCA+XMG+XNA+XK
          CALL ECM3(TCA,TMG,TNA,TK,TCL,TSO4,THCO3,TCO3,EC)
          H=10.**(-PH)
          ACT1=ACT(1.,EC)
          ACT2=ACT(2.,EC)
  * FIRST ION ACTIVITY APPROXIMATION.
          ASO4=TSO4*ACT2
          AK=TK*ACT1
          ANA=TNA*ACT1/(1.+ASO4/KD9)
          ACA=TCA/(1./ACT2+KW/(KD3*ACT1*H)+ASO4/KD4)
          AMG=TMG/(1./ACT2+KW/(KD7*ACT1*H)+ASO4/KD8)
          ASO4=TSO4/(1./ACT2+ACA/KD4+AMG/KD8+ANA/(ACT1*KD9))
          DO 20 II=1,5
          PCO2=H*H*SP2/(ACA*KH*KA1*KA2)
          ACA=TCA/(1./ACT2+KA1*KH*PCO2/(KD2*ACT1*H)+KW/(KD3*ACT1*H)+
         #KA1*KA2*KW*PCO2/(KD1*H*H)+ASO4/KD4)
          AMG=TMG/(1./ACT2+KA1*KH*PCO2/(KD6*ACT1*H)+KW/(KD7*ACT2*H)+
         #KA1*KA2*KH*PCO2/(KD5*H*H)+ASO4/KD8)
          ANA=TNA/(1./ACT1+ASO4/(ACT1*KD9)+KA1*KA2*KH*PCO2/(KD10*ACT2*H*H))
   20     ASO4=TSO4/(1./ACT2+ACA/KD4+AMG/KD8+ANA/(ACT1*KD9))
          ZCA=SQRT(ACA)
          ZMG=SQRT(AMG)
          K1=ZMG*XCA/(ZCA*XMG)
          K2=ANA*XCA/(ZCA*XNA)
          K3=ZCA*XK/(AK*XCA)
          K4=ZMG*XK/(AK*XMG)
          K5=ANA*XMG/(ZMG*XNA)
          K6=ANA*XK/(AK*XNA)
          WRITE(16,64)SAMPLE,K1,K2,K3,K4,K5,K6
   64     FORMAT(A10,6F8.2)
   50     CONTINUE
          WRITE(16,100)
          WRITE(16,65)
   65     FORMAT(" WARNING!!! K1, K3 AND K4 MAY BE RECIPROCALS OF SELECT-")
          WRITE(16,66)
   66     FORMAT(" IVITY COEFFICIENTS REPORTED EARLIER BY ROBBINS et.al.")
          CLOSE(10)
          CLOSE(16)
   51     FORMAT("  PH VALUE IS TO LOW")
   52     FORMAT("  CATION, CL OR SO4 VALUES ARE TO LOW")
          END
          END$
  *******************************************************************
```